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(54) Process for the preparation of solid catalyst components for the polymerization of olefins

(57) Process for the preparation of a solid catalyst component for olefins polymerization comprising (1) a magnesium halide in active form, (2) a titanium compound, and (3) an electron-donor compound selected from particular 1,3-diethers, said process being carried out by reaction between the compounds from (1) to (3), and comprising at least two additions of electron-donor (3) in the following order:

a) one addition prior to or during a reaction with (2) or with a halogenated compound, and then

b) one addition prior to or during a further reaction with (2).

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Description

The present invention concerns a process for the preparation of solid catalyst components.

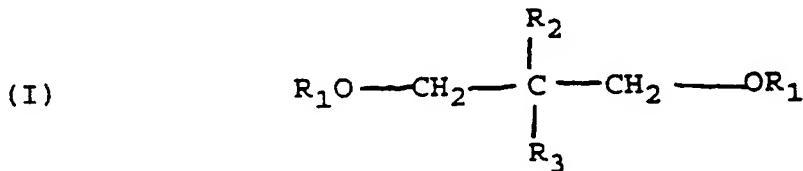
Published European patent application No. 361 494 describes solid catalyst components comprising a magnesium halide in active form, and supported on the latter a titanium compound containing at least one Ti-halide bond and an internal electron-donor compound selected from the ethers containing two or more ether groups, and having particular reaction characteristics towards the magnesium chloride and the $TiCl_4$.

The catalysts obtained from the above mentioned catalyst components, by way of reaction of the latter with an aluminum alkyl compound, exhibit high activity and stereospecificity in the polymerization of olefins, and do not require the use of external electron-donors.

According to published European patent application No. 361494, the internal electron-donor is introduced by performing only one addition of the electron-donor itself in one of the stages of the preparation of the solid catalyst component, generally prior to or during the reaction with the titanium compound.

It has now been found that if in the preparation of the above mentioned solid catalyst components one makes at least two successive electron-donor additions in the proper order, one obtains solid catalyst components capable of conferring to the catalyst obtained from them an improved activity/stereospecificity balance in the polymerization of olefins.

Therefore, one of the objects of the present invention is a process for the preparation of a solid catalyst component comprising (1) a magnesium halide in active form, and, supported thereon, (2) a titanium compound having at least one Ti-halogen bond, and (3) an electron-donor compound selected from the group consisting of the 1,3-diethers (3.1) having the general formula:



30 where R_1 , R_2 and R_3 , equal or different, are C_1 - C_{18} linear or branched alkyl, C_3 - C_{18} cycloaliphatic, C_6 - C_{18} aryl, C_7 - C_{18} alkylaryl or C_7 - C_{18} aralkyl radicals, and R_2 or R_3 can also be hydrogen atoms; or from the 1,3-diethers (3.2) where the carbon atom in position 2 belongs to a cyclic or polycyclic structure constituted by 5, 6, or 7 carbon atoms, or 5-n or 6-n' carbon atoms and n atoms of nitrogen and heteroatoms selected from the group consisting of N, O, S and Si respectively, where n is 1 or 2, and n' is 1, 2 or 3, said structure containing two or three unsaturations (cyclopolyenic structure) and optionally being condensed with other cyclic structures, or substituted with one or more substituents selected from the group consisting of linear or branched C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} aralkyl, C_7 - C_{20} alkylaryl radicals, and halogens, or being condensed with other cyclic structures and substituted with one or more of the above mentioned substituents that can also be bonded to the condensed cyclic structures; one or more of the above mentioned alkyl, cycloalkyl, aryl, aralkyl or alkylaryl radicals and the condensed cyclic structures optionally containing one or more heteroatoms as substitutes for the carbon or hydrogen atom, or both. The said process is carried out by way of reacting the magnesium halide (1) or one of its precursor, with the titanium compound (2) and the electron-donor compound (3), the reaction with the titanium compound (2) being optionally preceded by a reaction with a halogenated compound, and comprising at least two electron-donors (3) additions in the following order:

45 a) an addition prior to or during a reaction with the titanium compound (2) or with a halogenated compound, and then
b) an addition prior to or during a further reaction with the titanium compound (2).

50 The catalysts obtained from the solid catalyst components prepared by the above mentioned process exhibit a stereospecificity substantially improved with respect to the catalysts obtained from the solid catalyst component prepared with the same internal electron-donor, but adding it only once. Said improved stereospecificity provides superior polymers of propylene and α -olefins, having high levels of crystallinity, and, therefore, improved mechanical properties.

Moreover, the activity of the catalyst obtained from the solid catalyst component prepared with the process of the present invention remains at very high levels, which makes said solid catalyst component very attractive for industrial use.

Furthermore, the process of the present invention has the advantage of being very simple, and can be conducted in the absence of solvents, with exception of the final washings of the solid catalyst component.

Therefore, it is preferable that at least addition b) of the electron-donor (3) be carried out in the absence of solvents.

More preferably, all the additions of electron-donor (3) are carried out in the absence of solvents.

It is also preferable to carry out addition b), and any succeeding ones, during the reaction or reactions with the titanium compound.

A surprising aspect of the present invention is that the above mentioned results can be obtained only by using internal electron-donor of the type described above. For example, by using for additions a) and b) an electron-donor selected from the aromatic carboxylic acids esters, there is no improvement in the performance of the final catalyst compared to the case where there is only one addition.

In particular, in the 1,3-diethers of formula (I) R₁ is an alkyl radical with 1-6 carbon atoms, and more particularly it is a methyl; moreover, when R₂ is methyl, ethyl, propyl, or isopropyl, R₃ can be ethyl, propyl, isopropyl, butyl, isobutyl, 10 tert-butyl, 2-ethylhexyl, isopentyl, cyclopentyl, cyclohexyl, methyliclohexyl, phenyl or benzyl; when R₂ is hydrogen, R₃ can be ethyl, butyl, sec-butyl, tert-butyl, 2-ethylhexyl, cyclohexylethyl, diphenylmethyl, p-chlorophenyl, 1-naphthyl, 1-decahydronaphthyl; moreover R₂ and R₃ can be equal, and be ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, isopentyl, neopentyl, phenyl, benzyl, cyclohexyl, cyclopentyl.

Specific examples of 1,3-diethers advantageous for use are:

15 2-(2-ethylhexyl)-1,3-dimethoxypropane, 2-isopropyl-1,3-dimethoxypropane, 2-butyl-1,3-dimethoxypropane, 2-sec-butyl-1,3-dimethoxypropane, 2-cyclohexyl-1,3-dimethoxypropane, 2-phenyl-1,3-dimethoxypropane, 2-tert-butyl-1,3-dimethoxypropane, 2-cumyl-1,3-diethoxypropane, 2-(2-phenylethyl)-1,3-dimethoxypropane, 2-(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-(p-chlorophenyl)-1,3-dimethoxypropane, 2-(diphenylmethyl)-1,3-dimethoxypropane, 2-(1-naphthyl)-1,3-dimethoxypropane, 2-(p-fluorophenyl)-1,3-dimethoxypropane, 2-(1-decahydronaphthyl)-1,3-dimethoxypropane, 20 2-(p-tert-butylphenyl)-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2,2-diethyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane, 2,2-dibutyl-1,3-dimethoxypropane, 2,2-diethyl-1,3-diethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-diethoxypropane, 2,2-dibutyl-1,3-diethoxypropane, 2,2-methyl-2-ethyl-1,3-dimethoxypropane, 2-methyl-2-propyl-1,3-dimethoxypropane, 2-methyl-2-benzyl-1,3-dimethoxypropane, 2-methyl-2-methyl-1,3-dimethoxypropane, 25 2-methyl-2-phenyl-1,3-dimethoxypropane, 2-methyl-2-cyclohexyl-1,3-dimethoxypropane, 2-methyl-2-methylcyclohexyl-1,3-dimethoxypropane, 2,2-bis(p-chlorophenyl)-1,3-dimethoxypropane, 2,2-bis(2-phenylethyl)-1,3-dimethoxypropane, 2,2-bis(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-methyl-2-isobutyl-1,3-dimethoxypropane, 2-methyl-2-(2-ethylhexyl)-1,3-dimethoxypropane, 2,2-bis(2-ethylhexyl)-1,3-dimethoxypropane, 2,2-bis(p-methylphenyl)-1,3-dimethoxypropane, 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-diphenyl-1,3-dimethoxypropane, 2,2-dibenzyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-30 bis(cyclohexylmethyl)-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-diethoxypropane, 2,2-diisobutyl-1,3-dibutethoxypropane, 2-isobutyl-2-isopropyl-1,3-dimethoxypropane, 2,2-di-sec-butyl-1,3-dimethoxypropane, 2,2-di-tert-butyl-1,3-dimethoxypropane, 2,2-di-neopentyl-1,3-dimethoxypropane, 2-isopropyl-2-isopentyl-1,3-dimethoxypropane, 2-phenyl-2-benzyl-1,3-dimethoxypropane, 2-cyclohexyl-2-cyclohexylmethyl-1,3-dimethoxypropane.

The above 1,3-diethers of formula (I) (i.e., the 1,3-diethers (3.1)) and their methods of preparation are described in 35 published European patent application No. 361 494.

Preferably the carbon atoms in positions 1 and 3 in the 1,3-diethers (3.2) are secondary.

The substituents defined above for the 1,3-diethers (3.2) are preferably selected from the group consisting of linear or branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ aralkyl and C₇-C₂₀ alkylaryl radicals; Cl and F.

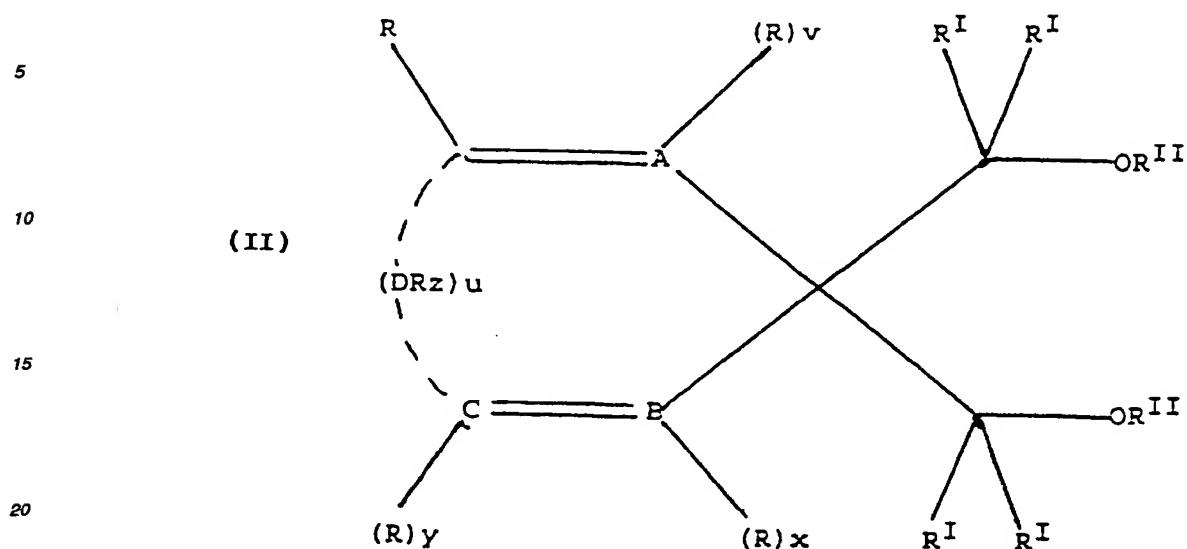
The heteroatoms optionally present in the alkyl, cycloalkyl, aryl, aralkyl, alkylaryl radicals and/or in the condensed 40 cyclic structures which are comprised in the 1,3-diethers (3.2) are preferably selected from the group consisting of N; O; S; P; Si and halogens, in particular Cl and F.

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Particularly preferred among the above 1,3-diethers are the compounds of formula:



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i) A, B, and C are carbon atoms and v, x, and y are equal to 1; or
 ii) A is a nitrogen atom, B and C are carbon atoms, v is equal to 0, and x and y are equal to 1; or
 iii) A and B are nitrogen atoms, C is a carbon atom, v and x are equal to 0, and y is equal to 1; or
 iv) A and B are carbon atoms, C is a nitrogen atom, v and x are equal to 1, and y is equal to 0;

when u = 1:

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i') A, B, C, and D are carbon atoms, v, x, and y are equal to 1, and z is equal to 2; or
 ii') A and B are carbon atoms, C is a nitrogen atom, D is an oxygen atom, v and x are equal to 1, y and z are equal to 0; or
 iii') A, B, and C are carbon atoms, D is an oxygen, nitrogen, sulfur, or silicon atom, v, x, and y are equal to 1, and z is equal to 0 when D is an oxygen or sulfur atom, equal to 1 when D is a nitrogen atom, and equal to 2 when D is a silicon atom;

when u = 2:

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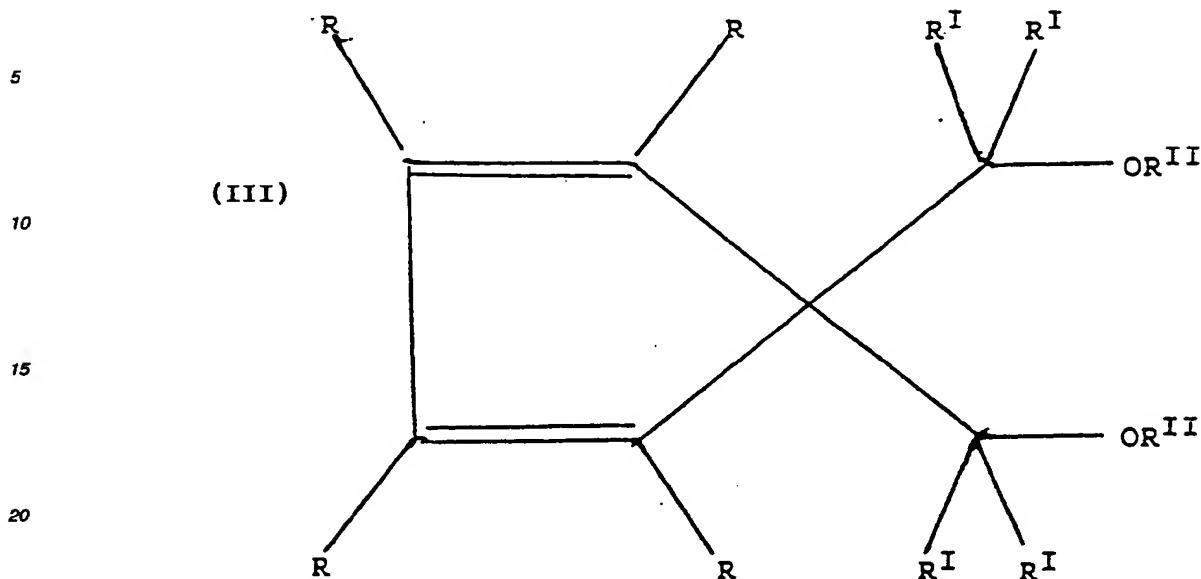
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A, B, and C are carbon atoms, D represents two carbon atoms bonded to each other by a single or double bond, v, x, and y are equal to 1, and z is equal to 1 when the couple of carbon atoms D is bonded by a double bond, and equal to 2 when said couple is bonded by a single bond; radicals R and RI, equal or different, are selected from the group consisting of hydrogen; halogens, preferably Cl and F; C₁-C₂₀ alkyl radicals, linear or branched; C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ aralkyl radicals; the RI radicals, equal or different, are selected from the group consisting of C₁-C₂₀ alkyl radicals, linear or branched; C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ aralkyl radicals, and two or more of the R radicals can be bonded to each other to form a condensed cyclic structure, saturated or unsaturated, optionally substituted with RIII radicals selected from the group consisting of halogens, preferably Cl and F; C₁-C₂₀ alkyl radicals, linear or branched; C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ aralkyl radicals; said radicals from R to RIII optionally containing one or more heteroatoms as substitutes for the carbon or hydrogen atom, or both.

Preferably in the compounds of formula (II) all the RI radicals are hydrogen, and each RI radical is methyl; the heteroatoms optionally present in the radicals from R to RIII are preferably selected from the group consisting of N; O; S; P; Si, and halogens, in particular Cl and F.

A preferred group of the compounds of formula (II) comprises the compounds of the general formula:



where the radicals from R to R''' are as defined above for formula (II).

In particular, two or more of the R radicals can be bonded to each other to form one or more condensed cyclic structures, preferably benzenic, optionally substituted by R''' radicals.

Specific examples of compounds comprised in formula (III) are:

1,1-bis(methoxymethyl)-cyclopentadiene;

30 1,1-bis(methoxymethyl)-2,3,4,5-tetramethylcyclopentadiene;

1,1-bis(methoxymethyl)-2,3,4,5-tetraphenylcyclopentadiene;

1,1-bis(methoxymethyl)-2,3,4,5-tetrafluorocyclopentadiene;

1,1-bis(methoxymethyl)-3,4-dicyclopentylcyclopentadiene;

1,1-bis(methoxymethyl)indene;

35 1,1-bis(methoxymethyl)-2,3-dimethylindene;

1,1-bis(methoxymethyl)-4,5,6,7-tetrahydroindene;

1,1-bis(methoxymethyl)-2,3,6,7-tetrafluoroindene;

1,1-bis(methoxymethyl)-4,7-dimethylindene;

1,1-bis(methoxymethyl)-3,6-dimethylindene;

40 1,1-bis(methoxymethyl)-4-phenylindene;

1,1-bis(methoxymethyl)-4-phenyl-2-methylindene;

1,1-bis(methoxymethyl)-4-cyclohexylindene;

1,1-bis(methoxymethyl)-7-(3,3,3-trifluoropropyl)indene;

1,1-bis(methoxymethyl)-7-trimethylsilylindene;

45 1,1-bis(methoxymethyl)-7-trifluoromethylindene;

1,1-bis(methoxymethyl)-4,7-dimethyl-4,5,6,7-tetrahydroindene;

1,1-bis(methoxymethyl)-7-methylindene;

1,1-bis(methoxymethyl)-7-cyclopentylindene;

1,1-bis(methoxymethyl)-7-isopropylindene;

50 1,1-bis(methoxymethyl)-7-cyclohexylindene;

1,1-bis(methoxymethyl)-7-tert-butylindene;

1,1-bis(methoxymethyl)-7-tert-butyl-2-methylindene;

1,1-bis(methoxymethyl)-7-phenylindene;

1,1-bis(methoxymethyl)-2-phenylindene;

55 1,1-bis(methoxymethyl)-1H-benz[e]indene;

1,1-bis(methoxymethyl)-1H-2-methylbenz[e]indene;

9,9-bis(methoxymethyl)fluorene;

9,9-bis(methoxymethyl)-2,3,6,7-tetramethylfluorene;

9,9-bis(methoxymethyl)-2,3,4,5,6,7-hexafluorofluorene;

9,9-bis(methoxymethyl)-2,3-benzofluorene;
9,9-bis(methoxymethyl)-2,3,6,7-dibenzofluorene;
9,9-bis(methoxymethyl)-2,7-diisopropylfluorene;
9,9-bis(methoxymethyl)-1,8-dichlorofluorene;
9,9-bis(methoxymethyl)-2,7-dicyclopentyfluorene;
9,9-bis(methoxymethyl)-1,8-difluorofluorene;
9,9-bis(methoxymethyl)-1,2,3,4-tetrahydrofluorene;
9,9-bis(methoxymethyl)-1,2,3,4,5,6,7,8-octahydrofluorene; and
9,9-bis(methoxymethyl)-4-tert-butylfluorene.

Other examples of 1,3-diethers (3.2) comprised in the definitions above are:

1,1-bis(1'-butoxyethyl)cyclopentadiene;
1,1-bis(1'-isopropoxy-n-propyl)cyclopentadiene;
1-methoxymethyl-1-(1'-methoxyethyl)-2,3,4,5-tetramethylcyclopentadiene;
1,1-bis(α -methoxybenzyl)indene;
1,1-bis(phenoxyethyl)indene;
1,1-bis(1'-methoxyethyl)-5,6-dichloroindene;
1,1-bis(phenoxyethyl)-3,6-dicyclohexylindene;
1-methoxymethyl-1-(1'-methoxyethyl)-7-tert-butylindene;
1,1-bis[2-(2'-methoxypropyl)]-2-methylindene;

3,3-bis(methoxymethyl)-3H-2-methylbenz[e]indene;
9,9-bis(α -methoxybenzyl)fluorene;
9,9-bis(1'-isopropoxy-n-butyl)-4,5-diphenylfluorene;
9,9-bis(1'-methoxyethyl)fluorene;
9-(methoxymethyl)-9-(1'-methoxyethyl)-2,3,6,7-tetrafluorofluorene;

9-methoxymethyl-9-pentoxyethylfluorene;
9-methoxymethyl-9-ethoxymethylfluorene;
9-methoxymethyl-9-(1'-methoxyethyl)fluorene;
9-methoxymethyl-9-[2-(2-methoxypropyl)]-fluorene.

1,1-bis(methoxymethyl)-2,5-cyclohexadiene;
1,1-bis(methoxymethyl)benzonaphthene;
7,7-bis(methoxymethyl)-2,5-norbornadiene;
9,9-bis(methoxymethyl)-1,4-methanediylbenzene;

4,4-bis(methoxymethyl)-4H-cyclopenta[d,e,f]phenanthrene;
9,9-bis(methoxymethyl)-9,10-dihydroanthracene;

7,7-bis(methoxymethyl)-7H-benz[d,e]anthracene;
1,1-bis(methoxymethyl)-1,2-dihydronaphthalene;
4,4-bis(methoxymethyl)-1-phenyl-3,4-dihydronaphthalene;
4,4-bis(methoxymethyl)-1-phenyl-1,4-dihydronaphthalene;
5,5-bis(methoxymethyl)-1,3,6-cycloheptatriene;

5,5-bis(methoxymethyl)-10,11-dihydro-5H-dibenzo[a,d] cycloheptene;
5,5-bis(methoxymethyl)-5H-dibenzo[a,d]cycloheptene;
9,9-bis(methoxymethyl)xanthene;
9,9-bis(methoxyisobutyl)thioxanthene;

4,4-bis(methoxymethyl)-1,4-pyran;
9,9-bis(methoxymethyl)N-tert-butyl-9,10-dihydroacridine;
4,4-bis(methoxymethyl)-1,4-chromene;
4,4-bis(methoxymethyl)-1,2,4-oxazine;
1,1-bis(methoxymethyl)benzo-2,3,1-oxazine;

5,5-bis(methoxymethyl)-1,5-pyridine;
5,5-bis(methoxymethyl)-6,7-dimethyl-1,5-pyridine;
2,2-bis(methoxymethyl)-3,4,5-trifluoroisopyrrole;
4,4-bis(1'-methoxyethyl)benzo-N-phenyl-1,4-dihydropyridine.

55 The 1,3-diethers (3.2) used in the catalyst components of the present invention can be prepared by first synthesizing the cyclopolyendimethylol by reaction of the desired cyclopolyene with paraformaldehyde in the presence of sodium alcoholate (as described by B. WESSLEN, ACTA CHEM. SCAND. 21 (1967) 718-20), and then transforming the derived dimethylol into the corresponding diether by way of alkylation, cycloalkylation, or arylation, according to known techniques, such as by reaction of the derived dimethylol with an alkyl, cycloalkyl, or aryl halide in the presence of a strong base, such as NaH, in a suitable solvent, such as tetrahydrofuran.

As stated above, the process of the present invention is carried out by causing the above mentioned electron-donors (3) to react with the magnesium halide (1), or one of its precursor, and the titanium compound (2), where the reaction with the titanium compound (2) is optionally preceded by a reaction with a halogenated compound.

The precursors of the magnesium halide are compounds which are capable of forming the magnesium halide in active form by reaction with a halogenated compound and/or a titanium compound (2).

Examples of the above mentioned precursors are:

- Grignard RMgX compounds where R is a C₁-C₂₀ hydrocarbon radical, such as C₁-C₂₀ alkyl or C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl or C₇-C₂₀ aralkyl; X is halide, preferably Cl;
- MgR₂ compounds where R is as defined above;
- MgCl₂ · nROH adducts where n generally ranges from 1 to 3, and R is as defined above;
- Mg(OR)₂ compounds where R is as defined above;
- X_nMg(OR)_{2-n} compounds where 0 < n < 2 and X and R are as defined above;
- complexes of magnesium halide with titanium alcoholates.

The titanium compound (2) is preferably selected from the titanium halides and halogen alcoholates, such as TiCl₃OR where R is, for example, a C₁-C₂₀ alkyl or a phenyl radical.

Titanium tetrachloride is the preferred compound.

Preferred examples of halogenated compounds are the silicon compounds containing halogens, in particular chlorine.

Examples of said compounds are compounds of the formula SiX_{4-n}Y_n, where X and Y are halogen atoms, and n is a number from 0 to 3, such as SiCl₄, the chlorosiloxanes of formula Si_nO_{n-1}Cl_{2n+2}, where n is a number from 2 to 7, for example Si₂OCl₆; halogenated polysilanes of formula Si_nX_{n+2}, where X is a halide and n is a number from 2 to 6, such as Si₄Cl₁₀; alkyl-halogenosilanes of the formula R_{4-n}SiX_n where R is a C₁-C₂₀ aliphatic or aromatic radical, X is halide, and n is a number from 1 to 3, such as C₂H₅SiCl₃, (CH₃)₃SiCl₂; halogenated alcoxanes of formula Si(OR)_{4-n}X_n where X is halide, R is a C₁-C₂₀ alkyl or an aryl radical, and n is a number from 1 to 3, such as Si(O₂C₂H₅)Cl₃.

Other examples of halogenated compounds are the hydrohalogenenic acids, such as HCl and thionyl chloride.

The silicon tetrachloride is particularly preferred among the halogenated compounds.

Examples of solvents that can be used in the process of the present invention are aliphatic, cycloaliphatic, aromatic or chlorinated hydrocarbon solvents such as hexane, heptane, cyclohexane, toluene, ethylbenzene, chlorobenzene, and dichloroethane.

The reactions between compounds (1), (2), and (3), and optionally the halogenated compound, can be carried out according to methods known in the art. The reaction order is not particularly critical.

However, as stated above, the reaction with the halogenated compound, that is normally used to convert the precursors into magnesium halides, is carried out prior to the reaction with the titanium compound (2).

In addition to the compounds and reactions described above it is also possible to use the compounds and reactions known in the art during the preparation of the solid catalyst component according to the process of the present invention.

The Mg/electron-donor (3) molar ratio used in the reactions mentioned above preferably ranges from 4:1 to 12:1 for additions a) and b) as well as any further addition. The quantity of electron-donor (3) used in said additions can be equal or different.

The titanium compound (2) is preferably used in molar excess with respect to the total quantity of magnesium halide (1), or its precursor, and electron-donor (3).

The reactions with titanium compound (2), the additions of electron-donor (3), and the reaction of the same with other compounds are preferably carried out at temperatures ranging from 0 to 135°C.

After addition b), or at any rate after the last addition of electron-donor (3), it is preferable to carry out another reaction with titanium compound (2) under the conditions described above.

Below are given some specific examples of process of preparing of the solid catalyst component, which in itself constitutes one of the objects of the present invention.

According to a variant of the process of the present invention, the magnesium halide (used anhydrous, containing less than 1% water), the titanium compound, and the electron-donor (3) are milled together under conditions that cause the activation of the magnesium halide; the milled product is then caused to react one or more times with the TiCl₄ in excess, optionally in the presence of an electron-donor (3), at a temperature ranging from 80 to 135°C. The solid obtained is separated, caused to react with excess TiCl₄ at temperatures ranging from 80 to 135°C, separated again, and then repeatedly washed with a hydrocarbon (hexane, for example) until no more chlorine ions can be detected in the wash liquid.

According to another method the anhydrous magnesium halide is preactivated according to known methods and then reacted with an excess of TiCl₄ containing the electron-donor (3), and optionally one of the above mentioned types of hydrocarbons. In this case also the operation takes place at a temperature ranging from 80° to 135°C. The reaction

with $TiCl_4$, in the presence of electron-donor (3), is repeated at least once. The solid is then separated, caused to react with $TiCl_4$ in excess at temperatures from 80 to 135°C, separated again and washed with hexane to eliminate all traces of nonreacted $TiCl_4$.

According to another method, a $MgCl_2 \cdot nROH$ adduct (particularly in the form of spheroidal particles) where n is generally from 1 to 3, and ROH is an alcohol, such as ethanol, butanol, isobutanol, is caused to react with an excess of $TiCl_4$ containing the electron-donor (3), and optionally one of the above mentioned types of hydrocarbon solvents. The reaction temperature initially is from 0 to 25°C, and then is increased to 80-130°C. After reaction, the solid is separated and caused to react once more with $TiCl_4$, in the presence of electron-donor (3), then it is separated, caused to react with $TiCl_4$ in excess at a temperature from 80 to 135°C, separated again and washed with a hydrocarbon until no chlorine ions are detected in the wash liquid.

According to yet another method, magnesium alcoholates or chloroalcoholates (the chloroalcoholates can be prepared particularly as described in USP 4,220,554) are caused to react at least twice with $TiCl_4$ in excess containing electron-donor (3), then the solid product is caused to react with $TiCl_4$ in excess and washed at a temperature from 80 to 135°C, operating under the reaction conditions described above.

According to another method, magnesium halide complexes with titanium alcoholates (the $MgCl_2 \cdot 2Ti(OC_4H_9)_4$ complex is a typical example) are caused to react, in a hydrocarbon solution, with $TiCl_4$ in excess containing the electron-donor (3) at a temperature ranging from 80 to 130°C; the solid product is separated and is reacted again with an excess of $TiCl_4$, in the presence of electron-donor (3) at temperatures ranging from 80 to 130°C, and then separated again and washed with hexane.

According to another method, the complex between $MgCl_2$ and the titanium alcoholate is caused to react in hydrocarbon solution with hydropolysiloxane; the solid product that is separated is caused to react at 50°C with silicon tetrachloride containing the diether; the solid is then caused to react with $TiCl_4$ in excess, in the presence of electron-donor (3) operating at 80-130°C. The solid product is separated, caused to react with $TiCl_4$ in excess at temperatures ranging from 80 to 135°C, separated again and then washed with hexane.

Electron-donor (3) is fixed on the magnesium halide in quantities generally ranging from 5 to 20% molar.

The Mg/Ti ratio in the catalyst components of the invention generally ranges from 30:1 to 4:1.

The reactions indicated above cause the formation of magnesium halide in active form. In addition to these reactions, other reactions are well known in the art that bring to the formation of magnesium halide in active form starting from magnesium compounds different from magnesium halides.

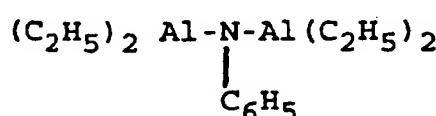
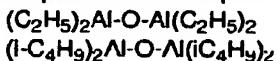
The active form of the magnesium halides in the catalyst components of the invention is recognizable by the fact that in the X-ray spectrum of the catalyst component the major intensity reflection which appears in the spectrum of the nonactivated magnesium halides (having surface area smaller than $3 m^2/g$) does not appear, and in its place there is a halo with the maximum intensity shifted with respect to the position of the major intensity reflection, or by the fact that the major intensity reflection has a mid-height width at least 30% greater than the one of the corresponding reflection of the nonactivated Mg halide. The most active forms are those in which the halo appears in the X-rays spectrum of the solid catalyst component.

Among the magnesium halides, the chloride is the preferred compound. In case of the most active forms of the magnesium chloride, the halo appears in place of the reflection which in the spectrum of the inactive magnesium halide is situated at the interplanar distance of 2.56 Å.

The catalyst components of the invention, by reaction with Al-alkyl compounds, form catalysts suitable for use in the polymerization of $CH_2=CHR$ olefins, where R is a hydrogen, or an alkyl radical with 1-6 carbon atoms, or an aryl radical, or mixtures of said olefins with each other and/or with diolefins.

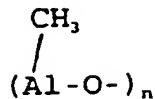
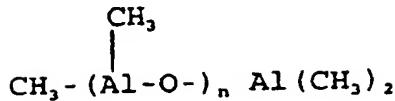
The Al-alkyl compounds comprise Al-trialkyls such as Al-triethyl, Al-triisobutyl, Al-tri-n-butyl and Al-trioctyl. Also suitable for use are the linear or cyclic Al-alkyl compounds containing two or more Al atoms bonded to each other by way of O, N, or S atoms.

Examples of said compounds are:



55





where n is a number between 1 and 20.

$\text{AlR}_2\text{OR}'$ compounds where R' is an $\text{C}_6\text{-C}_{20}$ aryl radical substituted at position 2 and/or 6, and R is a $\text{C}_1\text{-C}_6$ alkyl radical, can also be used as well as AlR_2H compounds, where R is a $\text{C}_1\text{-C}_6$ alkyl.

15 The Al-alkyl compound is used in Al/Ti mole ratios generally from 1 to 1000.

The trialkyl compounds can also be used in a mixture with Al-alkyl halides such as AlEt_2Cl and $\text{AlEt}_{3/2}\text{Cl}_{3/2}$.

The polymerization of olefins with the catalyst of this invention is carried out according to known methods operating in liquid phase, which consists of one or more olefin monomers, or a solution of one or more monomers in an aliphatic or aromatic hydrocarbon solvent, or in gas phase, or by a combination of liquid phase and gas phase.

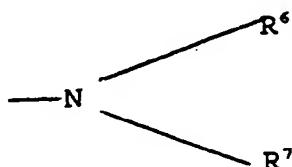
20 The (co)polymerization temperature usually ranges from 0° to 150°C ; in particular from 60° to 100°C . The polymerization occurs at atmospheric pressure or higher.

The catalysts can be precontacted with small quantities of olefins (prepolymerization). The prepolymerization improves the performance of the catalysts as well as the morphology of the polymers.

25 The prepolymerization is carried out by maintaining the catalysts in suspension in a hydrocarbon solvent (hexane or heptane, for example) adding an olefin, and operating at a temperature ranging from ambient temperature to 60°C , producing a quantity of polymer generally from 0.5 to 3 times the weight of the catalyst. The polymerization can also be carried out in liquid monomer, under the temperature conditions indicated above, thus producing quantities of polymer which can reach 1000 g for each g of catalyst component.

30 In the case of stereoregular polymerization of olefins, in particular the propylene, it may be best to use, together with the Al-alkyl compound, an external electron-donor preferably selected from the group of silicon compounds containing at least one SiOR bond (R = hydrocarbon radical); 2,2,6,6-tetramethylpiperidine; 2,6-diisopropylpiperidine; carboxylic acid esters, such as ethylparatoluate and ethylbenzoate; and the 1,3-diethers (3.1) and (3.2) defined above.

35 Preferably the silicon compounds have the formula $\text{R}^4{}_n\text{Si}(\text{OR}^5)_{4-n}$ where n is 1 or 2; the R^4 radical or radicals, equal or different, are selected from the group consisting of $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_3\text{-C}_{12}$ cycloalkyl, $\text{C}_6\text{-C}_{12}$ aryl, $\text{C}_7\text{-C}_{12}$ alkylaryl or $\text{C}_7\text{-C}_{12}$ aralkyl radicals;



45 radicals, where R^6 and R^7 , equal or different, have the same meaning as defined above for R^4 , or are bonded to each other to form a cyclic structure; radicals R^5 , equal or different, are a $\text{C}_1\text{-C}_6$ alkyl radical.

Optionally the radicals from R^4 to R^7 can contain one or more halogens, in particular Cl and F, as substitutes for the hydrogen atoms.

Examples of the silicon compounds include:

50 $(\text{tert-butyl})_2\text{Si}(\text{OCH}_3)_2$;
 $(\text{cyclohexyl})_2\text{Si}(\text{OCH}_3)_2$;
 $(\text{isopropyl})_2\text{Si}(\text{OCH}_3)_2$;
 $(\text{sec-butyl})_2\text{Si}(\text{OCH}_3)_2$;
 $(\text{cyclohexyl})(\text{methyl})\text{Si}(\text{OCH}_3)_2$;

55 $(\text{cyclopentyl})_2\text{Si}(\text{OCH}_3)_2$;
 $(\text{isopropyl})(\text{methyl})\text{Si}(\text{OCH}_3)_2$;
 $(\text{n-butyl})_2\text{Si}(\text{OCH}_3)_2$;
 $(\text{isobutyl})_2\text{Si}(\text{OCH}_3)_2$;
 $(\text{sec-butyl})_2\text{Si}(\text{OCH}_3)_2$;

(tert-butyl)(methyl)Si(OCH₃)₂;
 (tert-amyl)(methyl)Si(OCH₃)₂;
 (tert-hexyl)(methyl)Si(OCH₃)₂;
 (2-norbornyl)(methyl)Si(OCH₃)₂;
 5 (tert-butyl)(cyclopentyl)Si(OCH₃)₂;
 (2-norbornyl)(cyclopentyl)Si(OCH₃)₂;
 (tert-butyl)Si(OCH₃)₃;
 (tert-butyl)Si(OC₂H₅)₃;
 (2-norbornyl)Si(OCH₃)₃;
 10 (2-norbornyl)Si(OC₂H₅)₃;
 (tert-hexyl)Si(OCH₃)₃;
 (tert-hexyl)Si(OC₂H₅)₃;
 (tert-butyl)(2-methylpiperidyl)Si(OCH₃)₂;
 (tert-butyl)(3-methylpiperidyl)Si(OCH₃)₂;
 15 (tert-butyl)(4-methylpiperidyl)Si(OCH₃)₂;
 (tert-hexyl)(piperidyl)Si(OCH₃)₂;
 (tert-hexyl)(pyrrolidinyl)Si(OCH₃)₂;
 (methyl)(3,3,3-trifluoropropyl)Si(OCH₃)₂;
 (isopropyl)(3,3,3-trifluoropropyl)Si(OCH₃)₂;
 20 (n-butyl)(3,3,3-trifluoropropyl)Si(OCH₃)₂;
 (isobutyl)(3,3,3-trifluoropropyl)Si(OCH₃)₂;
 (sec-butyl)(3,3,3-trifluoropropyl)Si(OCH₃)₂;
 (tert-butyl)(3,3,3-trifluoropropyl)Si(OCH₃)₂;
 (3,3,3-trifluoropropyl)(piperidyl)Si(OCH₃)₂;
 25 (3,3,3-trifluoropropyl)(2-methylpiperidyl)Si(OCH₃)₂;
 (3,3,3-trifluoropropyl)(2-ethylpiperidyl)Si(OCH₃)₂;
 (3,3,3-trifluoropropyl)(3-methylpiperidyl)Si(OCH₃)₂;
 (3,3,3-trifluoropropyl)(4-methylpiperidyl)Si(OCH₃)₂; and
 (3,3,3-trifluoropropyl)₂Si(OCH₃)₂.

30 The molar ratio of the Al-alkyl compound to the external electron-donor generally is from 5:1 to 100:1, and preferably from 10:1 to 30:1; this ratio can be wider, for instance from 0.5:1 to 100:1, during the prepolymerization phase.

As already indicated, the catalysts find particular application in the polymerization of CH₂=CHR olefins where R is a 1-6 carbon alkyl or aryl radical. In particular, said catalysts are useful for the polymerization of propylene or its copolymerization with ethylene or other α -olefins.

35 The above catalysts are also useful for the production of polyethylenes and copolymers of ethylene with α -olefins, such as 1-butene, 1-hexene, and 1-octene.

The following examples are given in order to illustrate and not limit the invention.

In these examples unless otherwise indicated, the parts and percentages are expressed by weight.

The melt flow rate L (MFR/L) for the polypropylene is determined according to ASTM D 1238, condition L.

40 In order to determine the fraction of polymer insoluble in xylene at 25°C (X.I. %), 2.5 g of polymer are dissolved under agitation in 250 ml of xylene at 135°C, and after 20 minutes the content is allowed to cool to 25°C. After 30 minutes the precipitated polymer is filtered and dried at reduced pressure at 80°C until constant weight is reached.

Synthesis of the 9,9-bis(hydroxymethyl)fluorene

45 Into a 500 ml flask, in anhydrous atmosphere, are introduced in order: 100 ml of dimethyl sulfoxide (DMSO) distilled on CaH, 8 g of paraformaldehyde (rendered anhydrous at ambient temperature and at a pressure of 2 torr for 8 hours), and 1.4 g of sodium ethylate dissolved in 6 ml of ethanol.

After having cooled the suspension by placing the flask in an ice bath (the melt temperature of the DMSO/EtOH mixture is 13°C) and while maintaining the suspension under agitation, are added thereto over a period of thirty seconds, 100 ml of a solution of 16 g of fluorene in DMSO.

50 After 3 minutes from the beginning of the addition of the solution of fluorene in DMSO, the reaction is stopped by adding 1.5 ml of 37% aqueous HCl, and then the resulting mixture is diluted with 400 ml of water.

The mixture is saturated with NaCl, and 9,9-bis(hydroxymethyl)fluorene is extracted with ethyl acetate. The organic phase is then rendered anhydrous with anhydrous Na₂SO₄ and the solvent is flashed off. After crystallization by way of toluene, 15.2 g of product (yield: 70%) is obtained.

55 The ¹H-NMR spectrum of the product in CDCl₃, at 200 MHz and with tetramethylsilane (TMS) as internal standard, shows the following:

5	7.77 ppm, 7.62 ppm, 7.41 ppm, 7.32 ppm 3.99 ppm 0.25 ppm,	doublet, doublet, triplet, triplet, couplet, triplet,	2H aromatics 2H aromatics 2H aromatics 2H aromatics 4H CH ₂ 2H OH.
10			

15 Synthesis of 9,9-bis(methoxymethyl)fluorene

Into a 100 ml flask are introduced, in nitrogen atmosphere, in order: 30 ml of tetrahydrofuran (THF), 11.3 g of 9,9-bis(hydroxymethyl)fluorene, and 31.1 ml of CH₃I.

While agitating the flask content and operating at ambient temperature, one adds 4 g of NaH at 60% by weight in mineral oil over a period of 2 hours and 30 minutes and the mixture content is then allowed to react for 1 hour and 30 minutes.

The nonreacted CH₃I is recorded by way of distillation and the remaining content is diluted with 100 ml of water; the resulting floating solid is filtered and dried under vacuum at 40°C. After ethanol crystallization, 11.3 g of product (yield: 90%) is obtained.

25 The ¹H-NMR spectrum of the product in CDCl₃, at 200 MHz and with TMS as internal standard, shows the following:

30	7.75 ppm, 7.65 ppm, 7.39 ppm, 7.29 ppm, 3.64 ppm, 3.35 ppm,	doublet, doublet, triplet, triplet, singlet, singlet,	2H aromatics 2H aromatics 2H aromatics 2H aromatics 4H CH ₂ 6H CH ₃ .
35			

40 Example 1

Into a 500 ml cylindric glass reactor equipped with a filtering barrier and a stirrer are introduced at 0°C 225 ml of TiCl₄, and, while under agitation over a period of 15 minutes, 10.1 g (54 mmoles) of microspheroidal MgCl₂ · 2.1 C₂H₅OH obtained as described below.

At the end of the addition, the temperature of the reaction mixture is brought to 70°C, and 9 mmoles of 9,9-bis(methoxymethyl)fluorene are introduced (addition (a)).

The temperature is increased to 100°C and, after 2 hours, the TiCl₄ is removed by filtration. 200 ml of TiCl₄ (second addition) and 9 mmoles of 9,9-bis(methoxymethyl)fluorene are added (addition (b)); after 1 hour at 120°C the content is filtered again and another 200 ml of TiCl₄ are added, continuing the treatment at 120°C for one more hour; finally, the content is filtered and washed at 60°C with n-heptane until no chlorine ions are contained in the filtrate. The solid catalyst component obtained in this manner contains: Ti = 3.5% by weight; 9,9-bis(methoxymethyl)fluorene = 16.2% by weight.

The microspheroidal MgCl₂ · 2.1C₂H₅OH is prepared as follows.

55 48 g of anhydrous MgCl₂, 77 g of anhydrous C₂H₅OH, and 830 ml of kerosene are fed, in inert gas and at ambient temperature, into a 2 liter reactor equipped with a turbine agitator and in-line mixer. The content is heated to 120°C while stirring thus forming the MgCl₂ alcohol adduct that melts and remains mixed with the dispersing agent. The nitrogen pressure inside the reactor is maintained at 15 atm. The in-line mixer of the reactor is heated externally to 120°C

with a heating jacket, has an inside diameter of 1 mm, and is 3 meters long from one end of the heating jacket to the other.

Then the mixture is transferred through the pipe at a velocity of 7 m/sec ca.

At the exit of the pipe the dispersion is gathered in a 5 l flask, under agitation, containing 2.5 l of kerosene, and being externally cooled by way of a jacket maintained at an initial temperature of -40°C.

The final temperature of the emulsion is 0°C.

The spherical solid product that constituted the dispersed phase of the emulsion is separated by way of settling and filtration, and then washed with heptane and dried.

All these operations are carried out in an inert gas atmosphere.

10 130 g of $MgCl_2 \cdot 3C_2H_5OH$ in the form of spherical solid particles with a maximum diameter less than or equal to 50 micron are obtained.

The alcohol is removed from the product thus obtained at temperatures that are gradually increased from 50°C to 100°C in nitrogen atmosphere until the alcohol content is reduced to 2.1 moles per mole of $MgCl_2$.

15 Into a 4 liter reactor, previously purged for 1 hour with gaseous propylene at 70°C, are introduced, at ambient temperature and in propylene stream, 70 ml of anhydrous n-hexane containing 7 mmoles of aluminum triethyl and 4 mg of the solid catalyst component prepared as described above. The reactor is closed, 1.7 Nl of hydrogen and 1.2 kg of liquid propylene are introduced; the agitator is put in motion and the temperature of the reaction mixture is increased to 70°C over a period of 5 minutes. After 2 hours at 70°C, the agitation is stopped, the nonpolymerized monomer is removed, and the content is cooled to ambient temperature.

20 380 g of polypropylene are discharged from the reactor, said polypropylene having a fraction insoluble in xylene at 25°C (X.I.) = 97.7%, and MFR/L = 4.5 g/10 min. The polymer yield is 95,000 g of polypropylene/g of solid catalyst component.

Example 2

25 The procedure of example 1 is used, except in preparing the solid catalyst component, for additions a) and b) two parts equal to 9 mmoles each of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane are used instead of 9,9-bis(methoxymethyl)fluorene. The solid catalyst component thus obtained contains: Ti = 3.6% by weight; 2-isopropyl-2-isopentyl-1,3-dimethoxypropane = 12.7% by weight.

30 The polymerization is then carried out as described in Example 1, using 5.7 mg of solid catalyst component. 400 g of polypropylene is obtained, said polypropylene having X.I. = 98.0% and MFR/L = 5.1 g/10 min. The polymer yield is 70,000 g of polypropylene/g of solid catalyst component.

Example 3

35 Example 1 is repeated, except in preparing the solid catalyst component, for additions a) and b), two parts equal to 9 mmoles each of 2,2-diisobutyl-1,3-dimethoxypropane are used instead of 9,9-bis(methoxymethyl)fluorene. The product obtained contains: Ti = 2.8% by weight; 2,2-diisobutyl-1,3-dimethoxypropane = 14.7% by weight. Using 6.1 mg of solid catalyst component, 260 g of polypropylene is obtained having X.I. = 96.9%, and MFR/L = 4.9 g/10 min. The polymer yield is 42,600 g of polypropylene/g of catalyst component.

Example 4

40 Example 1 is repeated, except in preparing the solid catalyst component, for additions a) and b), two parts equal to 9 mmoles each of 2,2-diisopentyl-1,3-dimethoxypropane are used instead of 9,9-bis(methoxymethyl)fluorene. The product contains: Ti = 2.6% by weight; 2,2-diisopentyl-1,3-dimethoxypropane = 17.6% by weight. Using 7.3 mg of solid catalyst component, 332 g of polypropylene is obtained having X.I. = 95.2%, and MFR/L = 5.2 g/10 min. The polymer yield is 45,400 g of polypropylene/g of catalyst component.

Example 5

45 Example 1 is repeated, except in preparing of the solid catalyst component, for additions a) and b), two parts equal to 9 mmoles each of 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane are used instead of 9,9-bis(methoxymethyl)fluorene. The product obtained contains: Ti = 3.2% by weight; 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane = 13.2% by weight. Using 6.5 mg of solid catalyst component, 261 g of polypropylene is obtained having X.I. = 97.2%, and MFR/L = 5.9 g/10 min. The polymer yield is 40,200 g of polypropylene/g of catalyst component.

Comparative example 1

The procedure of example 1 is used, except in preparing the solid catalyst component the second addition of $TiCl_4$, addition b) of 9,9-bis(methoxymethyl)fluorene, and the subsequent reaction at $120^\circ C$ for 1 hour are omitted.

5 The preparation of the solid catalyst component is carried out as follows.

Into a 500 ml cylindrical glass reactor equipped with a filtering barrier are introduced at $0^\circ C$ 225 ml of $TiCl_4$, and, while under agitation over a period of 15 minutes, 10.1 g (54 mmoles) of microspheroidal $MgCl_2 \cdot 2.1C_2H_5OH$ obtained as described in Example 1.

10 At the end of the addition, the temperature is increased to $70^\circ C$, and 9 mmoles of 9,9-bis(methoxymethyl)fluorene are introduced.

The temperature is increased to $100^\circ C$, and, after 2 hours, the $TiCl_4$ is then removed by filtration. 200 additional ml of $TiCl_4$ are added continuing the treatment at $120^\circ C$ for an other hour; finally, the content is filtered and washed at $60^\circ C$ with n-heptane until no chlorine ions are contained in the filtrate.

15 The solid catalyst component obtained in this manner contains: Ti = 4% by weight; 9,9-bis(methoxymethyl)fluorene = 13.1% by weight.

Using 3.8 mg of the above mentioned solid catalyst component, 438 g of polypropylene is obtained having X.I. = 96.2%, and MFR/L = 4.9 g/10 min.

The polymer yield is 115,300 g of polypropylene/g of solid catalyst component.

Comparative Example 2

The procedure of Example 2 is used, except in preparing the solid catalyst component the second addition of $TiCl_4$, addition b) of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane, and the subsequent reaction at $120^\circ C$ for 1 hour are omitted.

25 The resulting solid catalyst component contains: Ti = 3.8% by weight; 2-isopropyl-2-isopentyl-1,3-dimethoxypropane = 11.1 by weight.

Using 5.1 mg of the above mentioned solid catalyst component 409 g of polypropylene are obtained having X.I. = 97.2%, and MFR/L = 5.9 g/10 min.

The polymer yield is 80,200 g of polypropylene/g of solid catalyst component.

Comparative Example 3

The procedure of Example 3 is used, except in preparing the solid catalyst component the second addition of $TiCl_4$, addition b) of 2,2-diisobutyl-1,3-dimethoxypropane, and the subsequent reaction at $120^\circ C$ for 1 hour are omitted.

35 The resulting solid catalyst component contains: Ti = 3.5% by weight; 2,2-diisobutyl-1,3-dimethoxypropane = 12.6% by weight.

Using 6.3 mg of the above mentioned solid catalyst component 349 g of polypropylene is obtained having X.I. = 95.2%, and MFR/L = 5.2 g/10 min.

The polymer yield is 55,400 g of polypropylene/g of solid catalyst component.

Comparative Example 4

The procedure of in Example 4 is used, except in preparing the solid catalyst component the second addition of $TiCl_4$, addition b) of 2,2-diisopentyl-1,3-dimethoxypropane, and the subsequent reaction at $120^\circ C$ for 1 hour are omitted.

45 The resulting solid catalyst component contains: Ti = 3.2% by weight; 2,2-diisopentyl-1,3-dimethoxypropane = 16.5% by weight.

Using 6.7 mg of the above mentioned solid catalyst component one obtains 403 g of polypropylene is obtained having X.I. = 93.6%, and MFR/L = 6.9 g/10 min.

The polymer yield is 60,100 g of polypropylene/g of solid catalyst component.

Comparative Example 5

The procedure of Example 5 is used, except in preparing the solid catalyst component the second addition of $TiCl_4$, addition b) of 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane, and the subsequent reaction at $120^\circ C$ for 1 hour are omitted.

55 The resulting solid catalyst component contains: Ti = 3.9% by weight; 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane = 11.5% by weight.

Using 7 mg of the above mentioned solid catalyst component 397 g of polypropylene is obtained having X.I. = 96.1%, and MFR/L = 6.3 g/10 min.

The polymer yield is 56,700 g of polypropylene/g of solid catalyst component.

Comparative Example 6

5 Into a 500 ml cylindric glass reactor equipped with a filtering barrier are introduced at 0°C 225 ml of $TiCl_4$, and, while under agitation over a period of 15 minutes, 10.1 g (54 mmoles) of microspheroidal $MgCl_2 \cdot 2.1 C_2H_5OH$ obtained as described in Example 1.

At the end of the addition, the temperature of the reaction mixture is increased to 40°C, and 9 mmoles of diisobutylphthalate are introduced.

10 The temperature of the reaction mixture is increased to 100°C in the course of one hour, and the stirring is continued for 2 more hours. Then the $TiCl_4$ is removed by filtration, 200 more ml of $TiCl_4$ are added, the stirring continues for 1 more hour at 120°C and finally the content is filtered and washed at 60°C with n-heptane until no chlorine ions are contained in the filtrate. The solid catalyst component obtained in this manner contains: Ti = 3.3% by weight; diisobutylphthalate = 8.2% by weight.

15 The polymerization is carried out as in Example 1, except that the hexane suspension introduced in the polymerization reactor is comprised of the following: 70 ml of anhydrous n-hexane, 7 mmoles of aluminum triethyl, 8.4 mg of the above mentioned solid catalyst component, and 0.35 mmoles of dicyclopentylmethoxysilane. 362 g of polypropylene is obtained, having X.I. = 98%, and MFR/L = 1.1 g/10 min.

The polymer yield is 43,100 g of polypropylene/g of solid catalyst component.

20 Comparative Example 7

25 Into a 500 ml cylindric glass reactor equipped with a filtering barrier are introduced at 0°C 225 ml of $TiCl_4$, and, while under agitation over a period of 15 minutes, 10.1 g (54 mmoles) of microspheroidal $MgCl_2 \cdot 2.1 C_2H_5OH$ obtained as described in Example 1.

At the end of the addition, the temperature of the reaction mixture is increased to 40°C, and 9 mmoles of diisobutylphthalate are introduced.

30 The temperature of the reaction mixture is increased to 100°C in the course of one hour, and the stirring is continued for 2 more hours. Then the $TiCl_4$ is removed by filtration, 200 more ml of $TiCl_4$ and 9 mmoles of diisobutylphthalate are added, the stirring continues for 1 more hour at 120°C and the $TiCl_4$ is removed by filtration. Then 200 more ml of $TiCl_4$ are added, the stirring is maintained for 1 hour at 120°C, and finally the content is filtered and washed at 60°C with n-heptane until no chlorine ions are contained in the filtrate. The solid catalyst component obtained in this manner contains: Ti = 3.1% by weight; diisobutylphthalate = 9.1% by weight.

35 The polymerization is carried out as in Comparative Example 6 using 8.1 mg of the above mentioned solid catalyst component. 326 g of polypropylene is obtained, having X.I. = 97.9%, and MFR/L = 1.2 g/10 min.

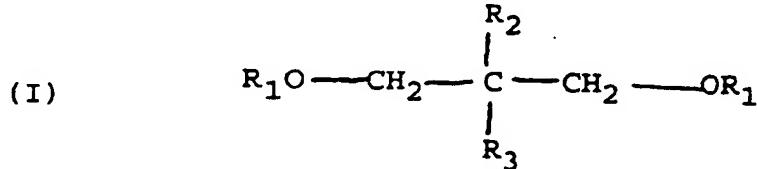
The polymer yield is 40,200 g of polypropylene/g of solid catalyst component.

A comparison of the data of comparative Examples 6 and 7 shows that if diisobutylphthalate is used in the process of this invention instead of the electron-donor (3) previously defined, it is not possible to obtain an increase in stereospecificity.

40

Claims

1. Process for the preparation of a solid catalyst component for the polymerization of olefins comprising (1) a magnesium halide in active form, and supported thereon (2) a titanium compound having at least one Ti-halogen bond, and (3) an electron-donor compound selected from the group consisting of the 1,3-diethers (3.1) having the general formula:



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where R_1 , R_2 and R_3 , equal or different, are C_1-C_{18} linear or branched alkyl, C_3-C_{18} cycloaliphatic, C_6-C_{18} aryl, C_7-C_{18} alkyaryl or C_7-C_{18} aralkyl radicals, and R_2 or R_3 can also be a hydrogen atom; or from the 1,3-diethers (3.2) where the carbon atom in position 2 belongs to a cyclic or polycyclic structure constituted by 5, 6, or 7 carbon atoms, or 5-n or 6-n' carbon atoms and n atoms of nitrogen and n' heteroatoms selected from the group consisting

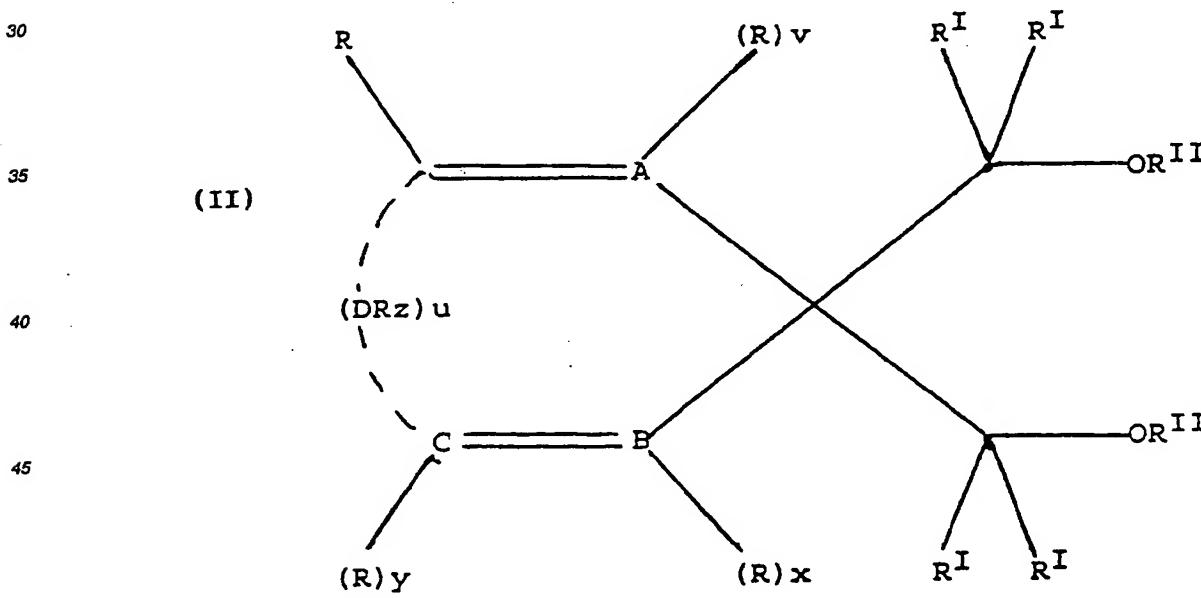
5 of N, O, S and Si respectively, where n is 1 or 2, and n' is 1, 2 or 3, said structure containing two or three unsaturations (cyclopolyenic structure) and optionally being condensed with other cyclic structures, or substituted with one or more substituents selected from the group consisting of linear or branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ aralkyl, C₇-C₂₀ alkylaryl radicals, and halogens, or being condensed with other cyclic structures and substituted with one or more of the above mentioned substituents that can also be bonded to the condensed cyclic structures; one or more of the above mentioned alkyl, cycloalkyl, aryl, aralkyl or alkylaryl radicals and the condensed cyclic structures optionally containing one or more heteroatoms as substitutes for the carbon or hydrogen atom, or both; said process being carried out by way of reacting the magnesium halide (1) or one of its 10 precursor, with the titanium compound (2) and the electron-donor compound (3), the reaction with the titanium (2) compound being optionally preceded by a reaction with a halogenated compound, and comprising at least two electron-donors (3) additions in the following order:

a) an addition prior to or during a reaction with the titanium compound (2) or with a halogenated compound, and then
 15 b) an addition prior to or during a further reaction with the titanium compound (2).

2. The process of claim 1, where in the 1,3-diethers of formula (I) R₁ is a C₁-C₆ alkyl radical; moreover, when R₂ is 20 methyl, ethyl, propyl, or isopropyl, R₃ can be ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, 2-ethylhexyl, isopentyl, cyclopentyl, cyclohexyl, methylcyclohexyl, phenyl or benzyl; when R₂ is hydrogen R₃ can be ethyl, butyl, sec-butyl, tert-butyl, 2-ethylhexyl, cyclohexylethyl, diphenylmethyl, p-chlorophenyl, 1-naphthyl, 1-decahydronaphthyl; R₂ and R₃ can also be equal, and be ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, isopentyl, neopentyl, phenyl, benzyl, cyclohexyl, cyclopentyl.

25 3. The process of claim 2, where the 1,3-diether is selected from the group consisting of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane; 2,2-diisobutyl-1,3-dimethoxypropane; 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane.

4. The process of claim 1, where the 1,3-diethers (3.2) are selected from the compounds of formula:



where A, B, C, and D, are carbon atoms or heteroatoms selected from the group consisting of N, O, Si and S; v, x, and y are 0 or 1; u and z are either 0, 1, or 2; provided that when u=0:

55 i) A, B, and C are carbon atoms and v, x, and y are equal to 1; or
 ii) A is a nitrogen atom, B and C are carbon atoms, v is equal to 0, and x and y are equal to 1; or
 iii) A and B are nitrogen atoms, C is a carbon atom, v and x are equal to 0, and y is equal to 1; or
 iv) A and B are carbon atoms, C is a nitrogen atom, v and x are equal to 1, and y is equal to 0;

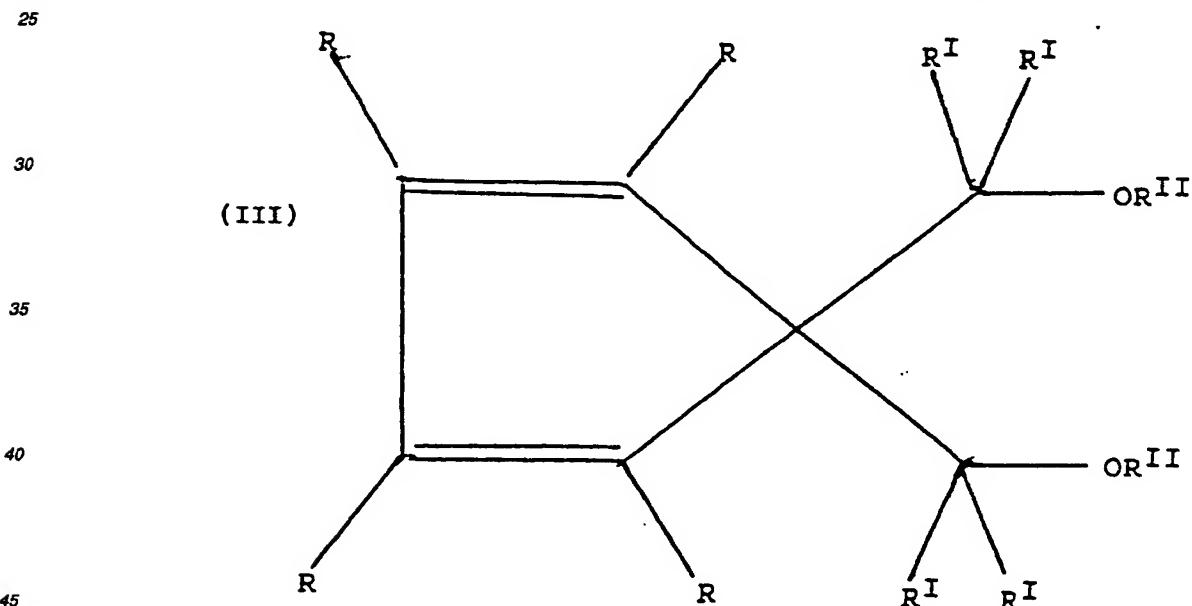
when $u = 1$:

5 i) A, B, C, and D are carbon atoms, v, x, and y are equal to 1, and z is equal to 2; or
 ii) A and B are carbon atoms, C is a nitrogen atom, D is an oxygen atom, v and x are equal to 1, y and z are equal to 0; or
 iii) A, B, and C are carbon atoms, D is an oxygen, nitrogen, sulfur, or silicon atom, v, x, and y are equal to 1, and z is equal to 0 when D is an oxygen or sulfur atom, equal to 1 when D is a nitrogen atom, and equal to 2 when D is a silicon atom;

10 when $u = 2$:

A, B, and C are carbon atoms, D represents two carbon atoms bonded to each other by a single or double bond, v, x, and y are equal to 1, and z is equal to 1 when the couple of carbon atoms D is bonded by a double bond, and equal to 2 when said couple is bonded by a single bond; radicals R and R^I, equal or different, are selected from the group consisting of hydrogen; halogens; C₁-C₂₀ alkyl radicals, linear or branched; C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ aralkyl radicals; the R^{II} radicals, equal or different, are selected from the group consisting of C₁-C₂₀ alkyl radicals, linear or branched; C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ aralkyl radicals, and two or more of the R radicals can be bonded to each other to form a condensed cyclic structure, saturated or unsaturated, optionally substituted with R^{III} radicals selected from the group consisting of halogens; C₁-C₂₀ alkyl radicals, linear or branched; C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ aralkyl radicals; said radicals from R to R^{III} optionally containing one or more heteroatoms as substitutes for the carbon or hydrogen atom, or both.

25 5. The process of claim 4, where the 1,3-diethers are selected from the compounds of formula:



30 where radicals R and R^I, equal or different, are selected from the group consisting of hydrogen; halogens; C₁-C₂₀ alkyl radicals, linear or branched; C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ aralkyl radicals; the R^{II} radicals, equal or different, are selected from the group consisting of C₁-C₂₀ alkyl radicals, linear or branched; C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ aralkyl radicals, and two or more of the R radicals can be bonded to each other to form a condensed cyclic structure, saturated or unsaturated, optionally substituted with R^{III} radicals selected from the group consisting of halogens; C₁-C₂₀ alkyl radicals, linear or branched; C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and aralkyl radicals; said radicals from R to R^{III} optionally containing one or more heteroatoms as substitutes for the carbon or hydrogen atom, or both.

35 6. The process of claim 5, where the 1,3-dioether (3.2) is selected from the group consisting of
 1,1-bis(methoxymethyl)-cyclopentadiene;
 1,1-bis(methoxymethyl)-2,3,4,5-tetramethylcyclopentadiene;
 1,1-bis(methoxymethyl)-2,3,4,5-tetraphenylcyclopentadiene;

1,1-bis(methoxymethyl)indene;
 1,1-bis(methoxymethyl)-2,3-dimethylindene;
 1,1-bis(methoxymethyl)-4,7-dimethylindene;
 1,1-bis(methoxymethyl)-4-phenyl-2-methylindene;
 5 1,1-bis(methoxymethyl)-7-(3,3,3-trifluoropropyl)indene;
 1,1-bis(methoxymethyl)-7-trimethylsilylindene;
 1,1-bis(methoxymethyl)-7-trifluoromethylindene;
 1,1-bis(methoxymethyl)-7-methylindene;
 10 1,1-bis(methoxymethyl)-7-cyclopentylindene;
 1,1-bis(methoxymethyl)-7-isopropylindene;
 1,1-bis(methoxymethyl)-7-cyclohexylindene;
 1,1-bis(methoxymethyl)-7-tert-butylindene;
 1,1-bis(methoxymethyl)-7-tert-butyl-2-methylindene;
 1,1-bis(methoxymethyl)-7-phenylindene;
 15 1,1-bis(methoxymethyl)-2-phenylindene;
 9,9-bis(methoxymethyl)fluorene;
 9,9-bis(methoxymethyl)-2,3,6,7-tetramethylfluorene;
 9,9-bis(methoxymethyl)-2,3,4,5,6,7-hexafluorofluorene;
 9,9-bis(methoxymethyl)-2,3-benzofluorene;
 20 9,9-bis(methoxymethyl)-2,3,6,7-dibenzofluorene;
 9,9-bis(methoxymethyl)-2,7-diisopropylfluorene;
 9,9-bis(methoxymethyl)-1,8-dichlorofluorene;
 9,9-bis(methoxymethyl)-2,7-dicyclopentylfluorene;
 9,9-bis(methoxymethyl)-1,8-difluorofluorene;
 25 9,9-bis(methoxymethyl)-1,2,3,4-tetrahydrofluorene;
 9,9-bis(methoxymethyl)-1,2,3,4,5,6,7,8-octahydrofluorene;
 and 9,9-bis(methoxymethyl)-4-tert-butylfluorene.

7. The process of claim 1, where the titanium compound (2) is selected from the group consisting of titanium halides
 30 and halogen alcoholates.

8. The process of claim 7, where the titanium compound (2) is titanium tetrachloride.

9. The process of claim 1, where the precursor of the magnesium halide (1) is selected from the group consisting of:
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- Grignard RMgX compounds where R is a C₁-C₂₀ hydrocarbon radical, and X is halide;
- MgR₂ compounds where R is as defined above;
- MgCl₂ · nROH adducts where n generally ranges from 1 to 3, and R is as defined above;
- Mg(OR)₂ compounds where R is as defined above;
- X_nMg(OR)_{2-n} compounds where 0 < n < 2 and X and R are as defined above;
- complexes of magnesium halide with titanium alcoholates.

40 10. The process of claim 1, where the halogenated compound is silicon tetrachloride.

45 11. The process of claim 1, where at least addition b) of electron-donor (3) is carried out without solvents.

12. The process of claim 1, where addition b), and other optional electron-donor (3) additions are carried out during the
 reaction or reactions with the titanium compound.

50 13. The process of claim 1, where the Mg/electron-donor (3) molar ratio ranges from 4:1 to 12:1 for both additions a)
 and b), and optional further additions.

14. The process of claim 1, where the reaction of the titanium compound (2), the addition of electron-donor (3), and the
 reaction of same with other compounds are carried out at temperatures ranging from 0 to 135°C.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 585 869 (MITSUI PETROCHEMICAL INDUSTRIES) * page 18, line 30; example 1 * * examples 9,10 * ---	1-3,7,8, 14	C08F10/00 C08F4/649
A	EP-A-0 451 645 (HIMONT) * claims 1,3 * * page 10, line 7 - line 8 * * page 5, line 6 - line 7 * -----	4	
TECHNICAL FIELDS SEARCHED (Int.Cl.6)			
C08F			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	6 June 1996	Fischer, B	
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